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## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : HITACHI METALS LTD

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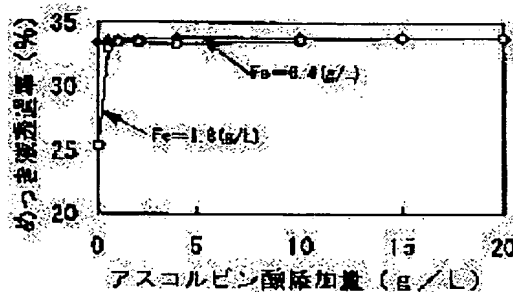
(72)Inventor : FURUICHI SHINJI  
SASAKI GAKUO  
FUJITA SEIJI

## (54) MAGNETIC PLATING FILM AND ITS PLATING METHOD

## (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a magnetic plating film having uniform composition preventing the turbidity of a plating solution, since the composition of the magnetic plating solution cannot be controlled due to the impossibility of precise measurement of the turbid plating solution by a spectrophotometer, when the plating solution containing much iron is used for

manufacturing the magnetic plating film having a high saturated magnetic flux density and a high specific resistance to be used for a thin film magnetic head, etc. **SOLUTION:** A turbidity preventive is added to a plating solution when the plating solution containing Fe within a range of 1.0-2.8 (g/L) or nickel and Fe in the metallic ion ratio within a range of 4-14 is used to form the magnetic plating film. Through these procedures, the transparency of the plating solution is sustained for preventing the production of a turbid matter so that the composition of the plating solution may be controlled at a specific value, thereby enabling the magnetic plating film having uniform composition to be formed.



## LEGAL STATUS

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## CLAIMS

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### [Claim(s)]

[Claim 1] The metal ion ratio of nickel and iron = (nickel/iron) magnetic plating film which is magnetic plating film of the permalloy formed using the plating liquid which is within the limits of 4-14, and is characterized by containing the range of nickel =35-60 (wt%) and iron =65-40 (wt%), and not including the turbidity object in plating liquid by adding a turbidity inhibitor in said plating liquid.

[Claim 2] Magnetic plating film which is magnetic plating film according to claim 1, and is characterized by adding and forming at least one or more kinds of components among cobalt, chromium, copper, and molybdenum at said plating liquid.

[Claim 3] Magnetic plating film which is magnetic plating film given in either of claims 1 or 2, and is characterized by said plating liquid containing iron in 1.0-2.8 (g/L).

[Claim 4] The metal ion ratio of nickel and iron = (nickel/iron) The amount of the plating component reduced by formation of the magnetic plating film is measured with a spectrophotometer using the plating liquid for forming the magnetic plating film which is within the limits of 4-14. The plating approach of the magnetic plating film characterized by a presentation forming the magnetic fixed plating film excluding a turbidity object by adding a turbidity inhibitor in said plating liquid, and maintaining the transparency of plating liquid in the plating approach of the magnetic plating film of filling up the plating component equivalent to the reduced amount.

[Claim 5] The plating approach of the magnetic plating film characterized by adding the organic compound which is water solubility and controls oxidation of the iron in plating liquid as a turbidity inhibitor in the plating liquid for forming the magnetic plating film of a permalloy, excluding a metal ion.

[Claim 6] said plating approach given in either of claims 4 or 5 -- the plating approach of the magnetic plating film characterized by being and using at least one or more of the ascorbic acid which has water solubility, protocatechuic-acid ester, propyl gallate, gallic-acid ethyl, a citric acid, an ascorbic-acid system compound, a protocatechuic-acid system compound, a gallic-acid system compound, and citric-acid system compounds as said turbidity inhibitor added in plating liquid.

[Claim 7] While preventing turbidity to either of claims 4 or 5, using an ascorbic acid, a citric acid or an ascorbic acid, and a citric acid as a turbidity inhibitor added in said plating liquid of a publication When PH of plating liquid is in an acidity side from a desired value, a water solution adds the sodium citrate which shows alkalescence, and PH of plating liquid is adjusted. It is the plating approach of the magnetic plating film which adds a hydrochloric acid or a sulfuric acid and is characterized by the thing of plating liquid to do for PH adjustment when PH is in an alkali side from a desired value.

[Claim 8] The plating approach of the magnetic plating film characterized by carrying out 0.5-20 (g/L) addition of the ascorbic acid as said turbidity inhibitor of a publication at either of claims 4 or 5.

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11-008/21

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the magnetic plating film which constitutes the magnetic pole or shielding of the head for record especially, and its plating approach about the magnetic plating film which constitutes the MR head used for magnetic recording media, such as a hard disk, and a thin film head.

[0002]

[Description of the Prior Art] In recent years, high coercive force and the magnetic head corresponding to the record medium of high density are called for more with the large capacity of the magnetic recording medium represented with a hard disk drive unit etc., and the request of a miniaturization. It was based on such needs and the structure of the magnetic head has shifted to the thin film head and the magneto-resistive effect mold magnetic head (an MR head is called hereafter) which use the thin film of the magnetic substance as a magnetic pole from the MIG head which uses the magnetic core of a ferrite.

[0003] The magnetic plating film which formed the magnetic substance excellent in soft magnetic characteristics, such as a permalloy containing many nickel, in the thin film by electroplating (plating is called hereafter) is used for the magnetic pole which constitutes the magnetic circuit of a thin film head or an MR head. When forming the thin film of several micron order, plating is used as the film production approach, because a film can be produced in a short time compared with a spatter etc. Even if it compares the plating film with the spatter film, it can acquire sufficient magnetic properties.

[0004] Generally, in nickel, 20 to 15 (wt%) extent is contained on the magnetic plating film used as the magnetic pole of a thin film head and an MR head, and the permalloy film of saturation-magnetic-flux-density  $B_s=0.95(T)$  and  $\rho$ = electrical resistivity 22 ( $\mu\Omega$  and cm) extent is used [ iron / 80-85 (wt%), and ] for it. Moreover, as for the presentation of the plating liquid which obtains this magnetic plating film, the thing of nickel / iron =25-50, or 0.3 to iron =0.5 (g/L) extent is used by the metal ion ratio of nickel and iron.

[0005]

[Problem(s) to be Solved by the Invention] With improvement in track recording density and the recording density of the truck cross direction, the coercive force of a record medium increases and the record frequency is also RF-ized further. For this reason, the magnetic pole is asked for their being high saturation magnetic flux density and high specific resistance more for reduction of the eddy current loss depending on increase and the record frequency of a record field. As a starting magnetic pole, the permalloy film which made [ many ] the iron ratio is suitable. It is the presentation which specifically contains nickel 35-60 (wt%) and iron 65-40 (wt%), and the permalloy film which has the property of saturation-magnetic-flux-density  $B_s=1.6(T)$  and  $\rho$ = electrical resistivity 55 ( $\mu\Omega$  and cm) extent is suitable. Here, the iron ratio will be carried out to to 65 (wt%) for it becoming difficult to maintain face centered cubic structure, and soft magnetic characteristics deteriorating, if the ratio of nickel is made under into 35 (wt%).

[0006] In order to form such permalloy film by plating, it is necessary to use the plating liquid which has a lot of iron ion compared with the permalloy of the conventional high nickel content. That is, it is possible to use the permalloy plating liquid of nickel / iron =4-14, or 1.0 to iron =2.8 (g/L) extent by the metal ion ratio of nickel and iron. A metal ion ratio shows the ratio of the

amount (g/L) of nickel added in plating liquid, and iron quantity (g/L) here. Moreover, a unit (g/L) shall say the number of grams of the metal contained in per 1l. of plating liquid. The relation of the nickel presentation in the magnetic plating film to the iron quantity in the plating liquid at the time of changing iron quantity and galvanizing by current density 10 (mA/cm<sup>2</sup>) and PH2.9 is shown using the amount of nickel in plating liquid as 13.5 (g/L) at drawing 9. In the presentation of this magnetic plating film, at the time of nickel =35 (wt%), when the iron quantity in plating liquid was 2.8 (g/L) and nickel =60 (wt%), the iron quantity in plating liquid was 1.0 (g/L).

Therefore, the number ratios of metal ions of nickel and iron equivalent to this range are nickel / about iron =4-14.

[0007] However, when iron ion concentration in plating liquid was made high, the problem that plating liquid became muddy and transparency fell generated iron ion in order to receive the oxidation from a hydroxyl group, the oxygen in air, etc. Furthermore, transparency falls further as it goes through time amount, after preparing plating liquid. Turbidity of plating liquid generated the problem to which it becomes difficult to measure the nickel ion concentration of plating liquid correctly with a spectrophotometer.

[0008] The property of the plating liquid permeability by measurement elapsed time is shown in drawing 5. Moreover, the nickel analysis value of the appearance at the time of surveying this plating liquid with a spectrophotometer to drawing 6 is shown. this plating liquid -- nickel =13.5 (g/L) -- as fixed -- iron = -- it is the case of 0.4 or 1.8 (g/L). Iron = although the plating liquid of 0.4 (g/L) does not almost have change of the permeability of plating liquid, the plating liquid of iron =1.8 (g/L) shows turbidity with time amount, and the permeability of plating liquid falls. Since the magnetic plating film is not formed in this measurement, the nickel and iron quantity in plating liquid do not change. When it measures with a spectrophotometer, an apparent nickel analysis value increases and it stops however, showing the amount of right nickel with the plating liquid with which iron =1.8 (g/L) became muddy. On the other hand, since there is no plating liquid of iron =0.4 (g/L), as for change of the permeability of plating liquid, a nickel analysis value is hardly changing, either. That is, it turns out that there is no difference in an apparent nickel analysis value and a true nickel analysis value.

[0009] The amount of the iron in conventional plating liquid and the relation of plating liquid permeability are shown in drawing 7. Moreover, the amount of the iron in conventional plating liquid and the relation of an apparent nickel analysis value are shown in drawing 8. drawing 7 and drawing 8 -- the nickel in plating liquid -- 13.5 (g/L) -- the turbidity degree of plating liquid to the amount of the iron in plating liquid when presupposing that it is fixed, carrying out 0-3 (g/L) addition of the iron, and leaving plating liquid in air at a room temperature for 20 hours was investigated. When the amount of the iron in plating liquid exceeds abbreviation 1.0 (g/L), it turns out that turbidity of plating liquid tends to take place.

[0010] In order to form the magnetic plating film of a fixed presentation, it is necessary to carry out the presentation of plating liquid to regularity. When plating liquid becomes muddy and measurement of the plating liquid presentation by the spectrophotometer becomes difficult, it becomes impossible to control uniformly the presentation of the plating liquid changed by formation of the magnetic plating film, and it becomes impossible that is, for a presentation to form the uniform magnetic plating film.

[0011] Detection of a plating liquid presentation becomes difficult by turbidity, and it becomes impossible moreover, for the plating equipment which performs automatically actuation which detects the presentation of plating liquid using a spectrophotometer, fills up the ion component which became insufficient, and carries out the presentation of plating liquid to regularity to fill up an ion component correctly. Then, the purpose of this invention prevents turbidity of the plating liquid to apply, and offers the magnetic plating film with a fixed presentation excluding a turbidity object.

[0012]

[Means for Solving the Problem] It is characterized by this invention obtaining the magnetic plating film with a fixed presentation in the plating of magnetic plating film, such as a permalloy, by containing 35-60 (wt%), and iron for nickel in 65-40 (wt%) by adding a turbidity inhibitor in the plating liquid which is within the limits of =(nickel/iron)4-14 in the metal ion ratio of nickel and iron. Moreover, it is characterized by adding at least one or more kinds in cobalt, chromium,

copper, and molybdenum in said plating liquid, and forming said magnetic plating film. Moreover, it is characterized by the plating liquid of said presentation containing iron in 1.0–2.8 (g/L).

[0013] The plating liquid for forming magnetic plating film, such as a permalloy whose metal ion ratio of nickel and iron is within the limits of  $=(\text{nickel}/\text{iron})4-14$ , is used for this invention. In the plating approach which measures with a spectrophotometer the amount of the plating component reduced by formation of the magnetic plating film, fills up said plating component to reduce, and controls the presentation of plating liquid A presentation is characterized by forming the magnetic fixed plating film by adding a turbidity inhibitor in said plating liquid, and maintaining the transparency of plating liquid. Moreover, it is characterized by adding at least one or more kinds in cobalt, chromium, copper, and molybdenum in said plating liquid, and forming said magnetic plating film. Moreover, it is characterized by the plating liquid of said presentation containing iron in 1.0–2.8 (g/L).

[0014] It is characterized by this invention using the organic compound which is water solubility and controls oxidation of the iron in plating liquid as a turbidity inhibitor added in plating liquid, excluding a metal ion in the plating of magnetic plating film, such as a permalloy. With moreover, the metal ion ratio of the plating liquid with which said plating liquid contains iron in 1.0–2.8 (g/L) or nickel, and iron  $= (\text{nickel}/\text{iron})$  it is characterized by being within the limits of 4–14.

[0015] This invention is characterized by using at least one or more of the ascorbic acid which has water solubility as said turbidity inhibitor, protocatechuic-acid ester, propyl gallate, gallic-acid ethyl, a citric acid, an ascorbic-acid system compound, a protocatechuic-acid system compound, a gallic-acid system compound, and citric-acid system compounds. Moreover, it is characterized by carrying out 0.5–20 (g/L) addition of the ascorbic acid as said turbidity inhibitor.

[0016] It is characterized by for this invention adding a hydrochloric acid or a sulfuric acid, and making it desired PH value, when the sodium citrate a water solution indicates alkalescence to be when PH of plating liquid is in an acidity side from a desired value, using an ascorbic acid, a citric acid or an ascorbic acid, and a citric acid as said turbidity inhibitor, while preventing turbidity is added, it adjusts to the value of a request of PH of plating liquid and PH is in an alkali side from a desired value.

[0017] An operation of this invention is described below. The plating liquid which made iron ion concentration high becomes muddy for the iron ion in plating liquid reacting with the oxygen in air, or reacting with other components in plating liquid, and generating a minute turbidity object. So, it is necessary first to control the reaction of iron ion, i.e., the operation which prevents oxidation, for the turbidity inhibitor added in plating liquid.

[0018] The following properties are required in order to use for a turbidity inhibitor further at plating. That is, in order to make it act on (1) ion, it is desirable to fulfill conditions, such as to constitute the ion or complex which tends to be incorporated by that it is water solubility, that the (2) turbidity inhibitor itself does not reduce the transparency of plating liquid, and (3) magnetism plating film, and not to change the presentation of the magnetic plating film. Magnetic plating film, such as a permalloy, can be formed without reducing transparency, even if iron ion concentration is high by adding organic compounds, such as an ascorbic acid which fulfills these conditions, in plating liquid. Furthermore, the magnetic plating film which uses a spectrophotometer, measures and controls the presentation of plating liquid correctly, and has a fixed presentation can be formed.

[0019] Moreover, a turbidity inhibitor may serve as functions, such as shock absorbing material which adjusts PH of plating liquid, at the same time it controls turbidity of plating liquid.

[0020]

[Embodiment of the Invention]

(Example 1) The nickel analysis value of the appearance of this plating liquid is shown for the plating liquid permeability by the addition of an ascorbic acid in drawing 1 at drawing 2. nickel =13.5 (g/L) in plating liquid — as fixed, the ascorbic acid was changed to 0.4 or the plating liquid which carried out 1.8 (g/L) addition and passed for 5 hours to 20 (g/L), and iron was added. Ascorbic acid = since the plating liquid of iron =0.4 (g/L) does not become muddy in the case of 0 (g/L), change does not take place to the permeability of plating liquid, and a nickel analysis value. On the other hand, since the plating liquid of iron =1.8 (g/L) has caused turbidity, the

permeability of plating liquid is low and the apparent nickel analysis value has come out highly. When carrying out 0.05 (g/L) addition of the ascorbic acid, there is no turbidity of plating liquid and the analysis value of apparent nickel shows an almost normal value. Although the ascorbic acid was added to 20 (g/L), change did not take place to permeability and an apparent nickel analysis value. Therefore, turbidity of plating liquid can be removed by adding an ascorbic acid more than 0.05 (g/L).

[0021] Furthermore, a plating liquid presentation is set to nickel =13.5 (g/L) and iron =1.8 (g/L) at drawing 3 and drawing 4, an ascorbic acid is added, plating liquid is put into air, and the stability of plating liquid is shown. With the plating liquid which carried out ascorbic-acid 0.05-0.5 (g/L) addition, when the permeability of plating liquid began to fall and 140 hours passed in about 10 hours, it became an additive-free case and the same value. With the plating liquid which carried out 1-20 (g/L) addition of the ascorbic acid, it turns out that it is not changeful to the permeability of plating liquid, and an apparent nickel analysis value even if 140 hours pass. Therefore, turbidity prevention of the long duration of plating liquid is possible in an ascorbic acid the range of 0.5-20 (g/L), and by adding in 1-20 (g/L) desirably, removing 0.5 (g/L). As mentioned above, the component of the plating liquid of this example 1 is shown in Table 1. It is indicated in Table 1 as the chemical used for plating liquid, and its amount of mixing. If it mixes at this rate, into plating liquid, nickel 13.5 (g/L) and Fe 1.8 (g/L) will be dissolved.

[0022]

[Table 1]

The amount of chemical name mixing (g/L)

NiSO<sub>4</sub>·6H<sub>2</sub>O 16.3 NiCl<sub>2</sub>·6H<sub>2</sub>O 39.9 FeSO<sub>4</sub>·7H<sub>2</sub>O 9.0 H<sub>3</sub>BO<sub>3</sub> 25.0 saccharin-sodium 1.5 ascorbic acids 0.05-20 [0023] (Example 2) The protocatechuic-acid ester, the propyl gallate, the gallic-acid ethyl, the citric acid, the protocatechuic-acid system compound, gallic-acid system compound, and citric-acid system compound other than an ascorbic acid can be used as a turbidity inhibitor of plating liquid. At least one or more may be used together out of these. However, having an antioxidizing operation with these organic compounds, since water solubility is not good, the organic compound unsuitable for a turbidity inhibitor is excepted. If it is the organic compound on which things other than these organic compounds also act as the organic compound equipped with an antioxidizing operation by water solubility, the complex which controls oxidation of iron ion by water solubility, or ion, it is available as a turbidity inhibitor of this invention. In Table 2, although the organic compound which has an antioxidizing function is shown, what is easy to melt into water can be used as a turbidity inhibitor.

[0024]

[Table 2]

The propriety ascorbic-acid C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> soluble as an organic compound molecular formula water solubility turbidity inhibitor Good protocatechuic-acid ester C<sub>9</sub>H<sub>10</sub>O<sub>4</sub> soluble Good propyl gallate C<sub>12</sub>H<sub>13</sub>O<sub>2</sub> soluble Good gallic-acid ethyl C<sub>9</sub>H<sub>11</sub>O<sub>2</sub> soluble Good citric-acid C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> soluble good isoamyl gallate C<sub>12</sub>H<sub>17</sub>O<sub>2</sub> refractory improper vitamin-E insoluble improper butyl hydroxy anisole C<sub>11</sub>H<sub>16</sub>O<sub>2</sub> insoluble improper -- sesamol C<sub>7</sub>H<sub>6</sub>O<sub>3</sub> -- refractory improper -- quercetin C<sub>7</sub>H<sub>6</sub>O<sub>3</sub> insoluble improper dibutyl oxy-toluene C<sub>15</sub>H<sub>24</sub>O -- insoluble improper -- nordihydroguaiaretic acid C<sub>18</sub>H<sub>22</sub>O<sub>4</sub> -- refractory improper guaiac resin -- insoluble [improper - - 0025] (Example 3) By the plating approach which adds an acid buffer to fluctuation of PH of the plating liquid by formation of the plating film, if only an ascorbic acid is put in too much so much as a turbidity inhibitor, the acidity of plating liquid will become strong with PHs 2-2.5, and desired PH value will no longer be acquired. While preventing turbidity using an ascorbic acid, a citric acid or an ascorbic acid, and a citric acid, when PH of plating liquid is in an acidity side from a desired value When a water solution adds the sodium citrate which shows alkalescence, and adjusts PH of plating liquid and PH has it in an alkali side from a desired value While preventing turbidity by adding the amount which adds a hydrochloric acid or a sulfuric acid, and adjusts PH of plating liquid, or falls an ascorbic acid within the range of 1-20 (g/L) in the total amount in plating liquid, plating liquid can be adjusted to about three PH.

[0026] (Example 4) In case iron is included in 1.0-2.8 (g/L) or the metal ion ratio of nickel and iron galvanizes the magnetic plating film using the plating liquid presentation for permalloys which is within the limits of =(nickel/iron)4-14 The turbidity inhibitor shown in an example 1 thru/or an



example 3 is added in plating liquid, the range of nickel =35-60 (wt%) and iron =65-40 (wt%) is contained, and a turbidity object is not incorporated, but the magnetic plating film with a fixed presentation is obtained. Moreover, magnetic properties may be raised while forming the magnetic plating film which does not contain a turbidity object by adding at least one or more kinds in cobalt, chromium, copper, and molybdenum in said plating liquid, and forming said magnetic plating film. Using the magnetic plating film which has these fixed presentations and does not contain a turbidity object, by forming the magnetic pole of a thin film head and an MR head, the record field of a magnetic pole is increased and eddy current loss can be reduced.

[0027] The plating equipment which forms such magnetic plating film is equipped with the tank which connects with the plating tub which fixes the wafer which forms the magnetic plating film, the spectrophotometer which measures the presentation of plating liquid, the plating liquid supply line and exhaust pipe way connected to a plating tub, and the two aforementioned ducts, and is made to circulate through plating liquid. Said a part of plating liquid supply line is a transparent glass tube, it is combined with a spectrophotometer and said glass tube serves as transparency of plating liquid, and a part which measures the amount of nickel and iron. The first container which supplies the water solution of first plating liquid component  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , and the second container which supplies the water solution of second plating liquid component  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  are combined with said tank. There is a duct which has the cock who performs and stops supply of the second plating liquid component in said first and second container for a start to said tank.

[0028] In above plating equipment, in case the magnetic plating film is formed in a wafer, the presentation of plating liquid is correctly measured with a spectrophotometer, the plating component reduced by formation of the magnetic plating film is supplied from said first or second container, and the presentation of plating liquid is fixed.

[0029] furthermore, the electromagnetism to which this invention opens and closes the cock of the second container with an electrical signal for a start [ said ] — automatic concentration accommodation of plating liquid can be performed by transposing to a closing motion valve and making said electrical signal transmit from said spectrophotometer. if it corresponds to a suitable threshold before falling so that the nickel concentration and iron concentration in plating liquid are inadequate for forming the magnetic plating film for which it asks — said electromagnetism — an electrical signal is transmitted to a closing motion valve, and plating liquid is supplemented with the said first or second plating liquid component. This supplement is performed within limits which return a plating liquid presentation.

[0030]

[Effect of the Invention] According to this invention, even if it uses plating liquid with the high ratio of iron ion, by controlling the fall of the transparency of plating liquid by the turbidity inhibitor, measuring a plating liquid presentation correctly with a spectrophotometer, and holding this presentation uniformly, a turbidity object cannot be incorporated but magnetic plating film, such as a permalloy which has a fixed presentation, can be formed.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The property of the ascorbic-acid addition by this invention, and plating liquid permeability

[Drawing 2] The property of the ascorbic-acid addition by this invention, and an apparent nickel analysis value

[Drawing 3] The property of measurement elapsed time and plating liquid permeability over an ascorbic-acid addition by this invention

[Drawing 4] The property of the nickel analysis value of the measurement elapsed time and appearance to an ascorbic-acid addition by this invention

[Drawing 5] The property of measurement elapsed time and plating liquid permeability over the iron quantity in conventional plating liquid

[Drawing 6] The property of the nickel analysis value of the measurement elapsed time and appearance to the iron quantity in conventional plating liquid

[Drawing 7] The iron quantity in conventional plating liquid, and the property of plating liquid permeability

[Drawing 8] The iron quantity in conventional plating liquid, and the property of an apparent nickel analysis value

[Drawing 9] The amount of the iron in conventional plating liquid, and the property of the nickel analysis value in the plating film

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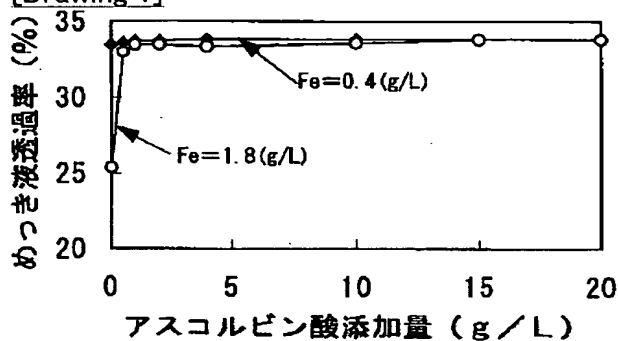
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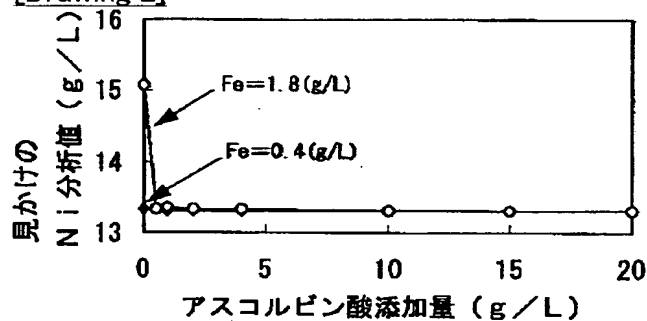
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## DRAWINGS

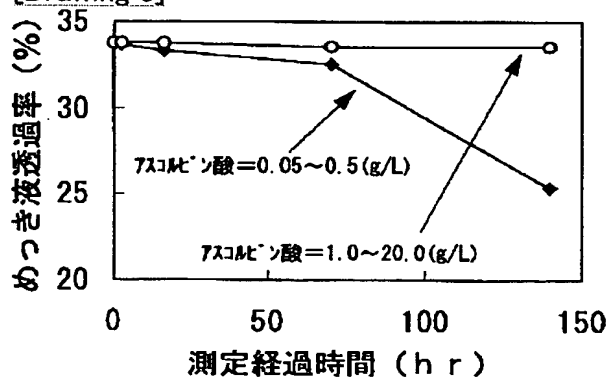
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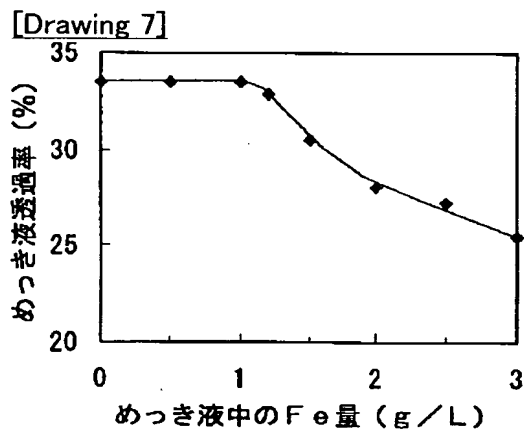
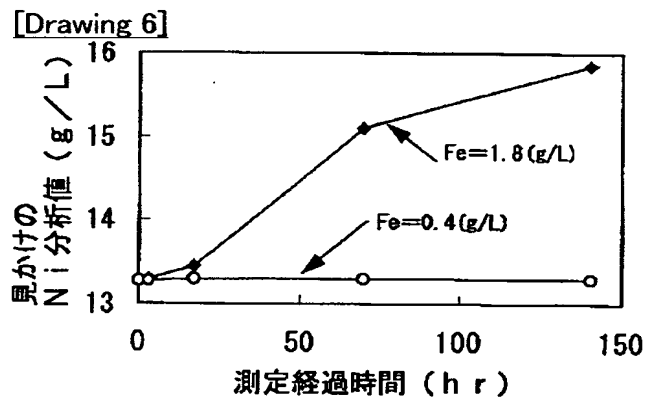
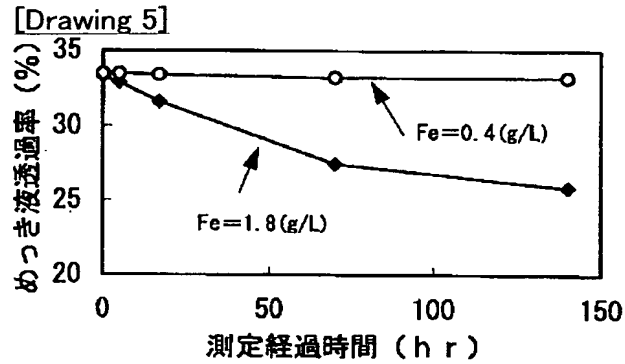
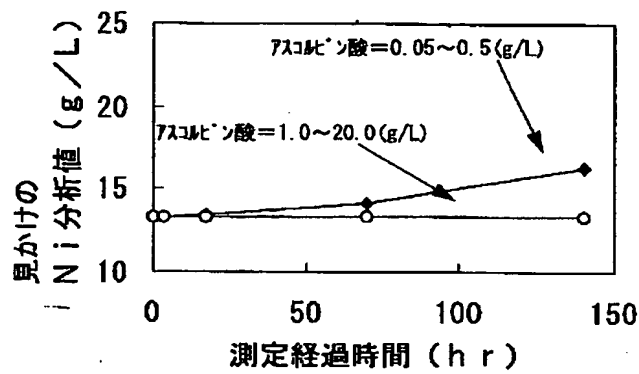
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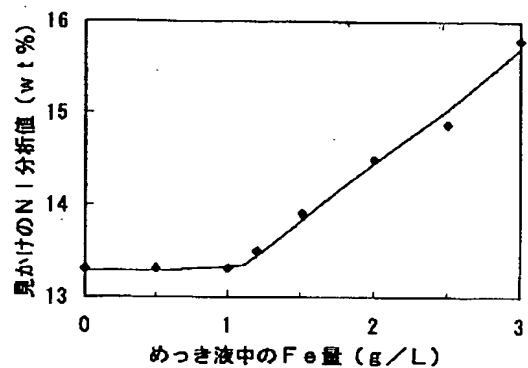
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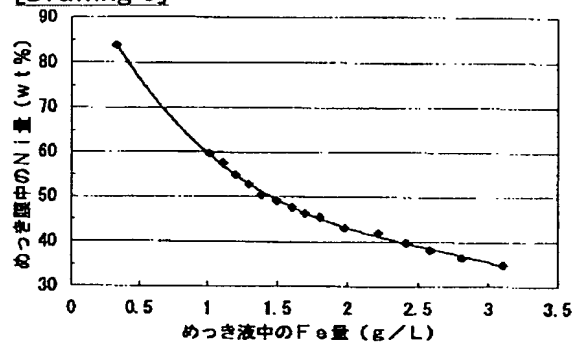
[Drawing 4]



[Drawing 8]



[Drawing 9]



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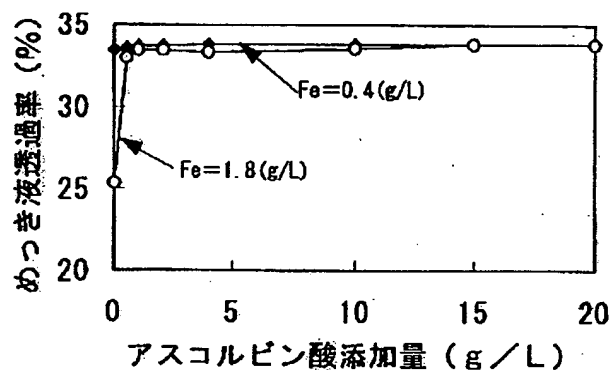
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(54)【発明の名称】 磁性めっき膜およびそのめっき方法

(57)【要約】

【課題】 薄膜磁気ヘッド等に用いる高飽和磁束密度、かつ高比抵抗の磁性めっき膜を製造するために、鉄を多く含むめっき液を用いると、めっき液が混濁して分光光度計によるめっき液組成の正確な測定ができず、磁性めっき膜の組成が制御出来なくなる。本発明の目的は係るめっき液の混濁を防止して均一な組成を有する磁性めっき膜を提供するものである。

【解決手段】 鉄を1.0~2.8 (g/L) の範囲で含み、あるいはニッケルと鉄の金属イオン比が(ニッケル/鉄) = 4~14の範囲内にあるめっき液を用いて磁性めっき膜を形成する際にめっき液に混濁防止剤を添加することによって、めっき液の透明度を維持して、且つ混濁物の発生を防止し、めっき液の組成を一定に調節して組成が均一な磁性めっき膜を形成することができる。



## 【特許請求の範囲】

【請求項1】ニッケルと鉄の金属イオン比が(ニッケル/鉄) = 4~14の範囲内であるめっき液を用いて形成するパーマロイの磁性めっき膜であって、前記めっき液に混濁防止剤を添加することにより、ニッケル=35~60 (wt%)、鉄=65~40 (wt%)の範囲を含有し、めっき液中の混濁物を含まないことを特徴とする磁性めっき膜。

【請求項2】請求項1に記載の磁性めっき膜であって、前記めっき液にコバルト、クロム、銅、モリブデンのうち少なくとも1種類以上の成分を添加して形成することを特徴とする磁性めっき膜。

【請求項3】請求項1または2のいずれかに記載の磁性めっき膜であって、前記めっき液が鉄を1.0~2.8 (g/L)の範囲で含むことを特徴とする磁性めっき膜。

【請求項4】ニッケルと鉄の金属イオン比が(ニッケル/鉄) = 4~14の範囲内である磁性めっき膜を形成するためのめっき液を用いて、磁性めっき膜の形成により低減しためっき成分の量を分光光度計で測定して、低減した量に相当するめっき成分を補充する磁性めっき膜のめっき方法において、前記めっき液に混濁防止剤を添加し、めっき液の透明度を維持することにより、混濁物を含まず組成が一定である磁性めっき膜を形成することを特徴とする磁性めっき膜のめっき方法。

【請求項5】パーマロイの磁性めっき膜を形成するためのめっき液に、混濁防止剤として金属イオンを含まず且つ水溶性であってめっき液中の鉄の酸化を抑制する有機化合物を添加することを特徴とする磁性めっき膜のめっき方法。

【請求項6】請求項4または5のいずれかに記載の前記めっき方法において、めっき液に添加する前記混濁防止剤として、水溶性を有するアスコルビン酸、プロトカテク酸エステル、没食子酸プロピル、没食子酸エチル、クエン酸、アスコルビン酸系化合物、プロトカテク酸系化合物、没食子酸系化合物、クエン酸系化合物のうち少なくとも一つ以上を用いることを特徴とする磁性めっき膜のめっき方法。

【請求項7】請求項4または5のいずれかに記載の前記めっき液に添加する混濁防止剤として、アスコルビン酸またはクエン酸もしくはアスコルビン酸とクエン酸を用いて混濁を防止するとともに、めっき液のPHが所望の値より酸性側にある場合は水溶液が弱アルカリ性を示すクエン酸ナトリウムを添加しめっき液のPHの調整を行い、PHが所望の値よりアルカリ側にある場合は、塩酸もしくは硫酸を添加しめっき液のPH調整することを特徴とする磁性めっき膜のめっき方法。

【請求項8】請求項4または5のいずれかに記載の前記混濁防止剤として、アスコルビン酸を0.5~2.0 (g/L)添加することを特徴とする磁性めっき膜のめっき

方法。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明はハードディスク等の磁気記録装置に用いるMRヘッドや薄膜ヘッドを構成する磁性めっき膜に関するものであり、特に記録用ヘッドの磁極あるいはシールドを構成する磁性めっき膜およびそのめっき方法に係るものである。

【0002】

【従来の技術】近年、ハードディスク装置等で代表される磁気記録装置の大容量および小型化の要請に伴い、より高保磁力かつ高密度の記録媒体に対応した磁気ヘッドが求められている。そのようなニーズに即して磁気ヘッドの構造はフェライトの磁気コアを用いるMIGヘッドから、磁性体の薄膜を磁極とする薄膜ヘッドおよび磁気抵抗効果型磁気ヘッド(以下、MRヘッドと称する)に移行している。

【0003】薄膜ヘッドあるいはMRヘッドの磁気回路を構成する磁極には、ニッケルを多く含有するパーマロイ等の軟磁気特性に優れた磁性体を電気めっき(以下、めっきと称する)で薄膜に形成した磁性めっき膜が使用されている。製膜方法としてめっきを用いるのは、数ミクロンオーダーの薄膜を形成する場合、スパッタ等比べて短時間で製膜できるためである。めっき膜はスパッタ膜と比較しても十分な磁気特性を得ることができる。

【0004】一般に、薄膜ヘッドおよびMRヘッドの磁極となる磁性めっき膜には、ニッケルを80~85 (wt%)、鉄を20~15 (wt%)程度を含有して、飽和磁束密度 $B_s = 0.95$  (T)、電気抵抗率 $\rho = 22$  ( $\mu\Omega \cdot \text{cm}$ )程度のパーマロイ膜が使用されている。また、この磁性めっき膜を得るめっき液の組成は、ニッケルと鉄の金属イオン比でニッケル/鉄=25~50、あるいは鉄=0.3~0.5 (g/L)程度のものが用いられている。

【0005】

【発明が解決しようとする課題】線記録密度およびトラック幅方向の記録密度の向上に伴い、記録媒体の保磁力が増大されて、さらに記録周波数も高周波化されている。このため、磁極には記録磁界の増大および記録周波数に依存する渦電流損の低減のために、より高飽和磁束密度かつ高比抵抗であることが求められている。係る磁極としては、鉄の比率を多くしたパーマロイ膜が適している。具体的にはニッケル35~60 (wt%)、鉄65~40 (wt%)を含有する組成であり、飽和磁束密度 $B_s = 1.6$  (T)、電気抵抗率 $\rho = 55$  ( $\mu\Omega \cdot \text{cm}$ )程度の特性を有するパーマロイ膜が好適である。ここで、鉄の比率を65 (wt%)までとしているのは、ニッケルの比率を35 (wt%)未満にすると面心立方構造を保つことが困難となり軟磁気特性が劣化するためである。

【0006】このようなパーマロイ膜をメッキで形成するには、従来の高ニッケル含有のパーマロイに比べて多量の鉄イオンを有するめっき液を用いることが必要になる。即ち、ニッケルと鉄の金属イオン比でニッケル/鉄 $=4\sim14$ 、あるいは鉄 $=1.0\sim2.8$  (g/L) 程度のパーマロイめっき液を用いることが考えられる。ここで金属イオン比とはめっき液に添加したニッケル量 (g/L) と鉄量 (g/L) の比を示す。また、単位 (g/L) はめっき液1リットルあたりに含まれる金属のグラム数をいうものとする。図9にめっき液中のニッケル量を13.5 (g/L) として、鉄量を変えて電流密度10 (mA/cm<sup>2</sup>)、PH2.9でめっきを行った場合のめっき液中の鉄量に対する磁性めっき膜中のニッケル組成の関係を示す。この磁性めっき膜の組成で、ニッケル $=35$  (wt%) のときはめっき液中の鉄量が2.8 (g/L)、ニッケル $=60$  (wt%) のときはめっき液中の鉄量が1.0 (g/L) であった。ゆえにこの範囲に相当するニッケルと鉄の金属イオン数比はニッケル/鉄 $=4\sim14$ 程度である。

【0007】しかし、めっき液中の鉄イオン濃度を高くすると、鉄イオンは水酸基や空気中の酸素などから酸化作用を受けるため、めっき液が混濁して透明度が低下するという問題が発生した。さらに、めっき液を調合してから時間を経過するに従い透明度は一層低下していく。めっき液が混濁すると、分光光度計でめっき液のニッケルイオン濃度を正確に測定することが困難になる問題が発生した。

【0008】図5に測定経過時間によるめっき液透過率の特性を示す。また、図6にこのめっき液を分光光度計で実測した場合の見かけのニッケル分析値を示す。このめっき液はニッケル $=13.5$  (g/L) 一定として、鉄 $=0.4$ または $1.8$  (g/L) の場合である。鉄 $=0.4$  (g/L) のめっき液は、めっき液の透過率の変化はほとんどないが、鉄 $=1.8$  (g/L) のめっき液は、時間と共に混濁を示し、めっき液の透過率が低下していく。この測定では磁性めっき膜の形成を行わないので、めっき液中のニッケル及び鉄量は変化しない。しかし、分光光度計で測定すると、鉄 $=1.8$  (g/L) の混濁しためっき液では見かけのニッケル分析値が増加し、正しいニッケル量を示さなくなる。一方、鉄 $=0.4$  (g/L) のめっき液は、めっき液の透過率の変化はほとんどない為、ニッケル分析値も変化していない。すなわち、見かけのニッケル分析値と真のニッケル分析値に差異がないことがわかる。

【0009】図7に従来のめっき液中の鉄の量とめっき液透過率の関係を示す。また、図8に従来のめっき液中の鉄の量と見かけのニッケル分析値の関係を示す。図7および図8はめっき液中のニッケルを13.5 (g/L) 一定として、鉄を0 $\sim$ 3 (g/L) 添加してめっき液を室温で空気中に20時間放置した時の、めっき液中

の鉄の量に対するめっき液の混濁度合いを調べた。めっき液中の鉄の量が略1.0 (g/L) を越えるとめっき液の混濁が起こり易いことが判る。

【0010】一定の組成の磁性めっき膜を形成するには、めっき液の組成を一定にする必要がある。即ち、めっき液が混濁して分光光度計によるめっき液組成の測定が困難になると、磁性めっき膜の形成によって変動するめっき液の組成を一定に制御することができなくなり、組成が均一な磁性めっき膜を形成することができなくなる。

【0011】また、分光光度計を用いてめっき液の組成を検知して、足りなくなったイオン成分を補充してめっき液の組成を一定にする動作を自動で行うめっき装置は、混濁によりめっき液組成の検知が困難となり、イオン成分の補充を正確に行えなくなる。そこで本発明の目的は係るめっき液の混濁を防止し、混濁物を含まず組成が一定な磁性めっき膜を提供するものである。

【0012】

【課題を解決するための手段】本発明は、パーマロイ等の磁性めっき膜のめっきにおいて、ニッケルと鉄の金属イオン比で (ニッケル/鉄) $=4\sim14$  の範囲内であるめっき液に混濁防止剤を添加することにより、ニッケルを35 $\sim$ 60 (wt%)、鉄を65 $\sim$ 40 (wt%) の範囲で含有して、組成が一定な磁性めっき膜を得ることを特徴とする。また、前記めっき液にコバルト、クロム、銅、モリブデンのうち少なくとも1種類以上を添加して前記磁性めっき膜を形成することを特徴とする。また、前記組成のめっき液が鉄を1.0 $\sim$ 2.8 (g/L) の範囲で含むことを特徴とする。

【0013】本発明は、ニッケルと鉄の金属イオン比が (ニッケル/鉄) $=4\sim14$  の範囲内であるパーマロイ等の磁性めっき膜を形成するためのめっき液を用いて、磁性めっき膜の形成により低減するめっき成分の量を分光光度計で測定して、前記低減するめっき成分を補充してめっき液の組成を制御するめっき方法において、前記めっき液に混濁防止剤を添加して、めっき液の透明度を維持することにより、組成が一定である磁性めっき膜を形成することを特徴とする。また、前記めっき液にコバルト、クロム、銅、モリブデンのうち少なくとも1種類以上を添加して前記磁性めっき膜を形成することを特徴とする。また、前記組成のめっき液が鉄を1.0 $\sim$ 2.8 (g/L) の範囲で含むことを特徴とする。

【0014】本発明はパーマロイ等の磁性めっき膜のめっきにおいて、めっき液に添加する混濁防止剤として、金属イオンを含まず、且つ水溶性であり、めっき液中の鉄の酸化を抑制する有機化合物を用いることを特徴とする。また、前記めっき液が鉄を1.0 $\sim$ 2.8 (g/L) の範囲で含むめっき液、或いはニッケルと鉄の金属イオン比で (ニッケル/鉄) $=4\sim14$  の範囲内であることを特徴とする。



【0015】本発明は前記混濁防止剤として水溶性を有するアスコルビン酸、プロトカテク酸エステル、没食子酸プロピル、没食子酸エチル、クエン酸、アスコルビン酸系化合物、プロトカテク酸系化合物、没食子酸系化合物、クエン酸系化合物のうち少なくとも一つ以上を用いることを特徴とする。また、前記混濁防止剤として、アスコルビン酸を0.5～20 (g/L) 添加することを特徴とする。

【0016】本発明は前記混濁防止剤として、アスコルビン酸またはクエン酸もしくはアスコルビン酸とクエン酸を用いて、混濁を防止するとともにめっき液のPHが所望の値より酸性側にある場合は水溶液が弱アルカリ性を示すクエン酸ナトリウムを添加しめっき液のPHを所望の値に調整を行い、PHが所望の値よりアルカリ側にある場合は塩酸もしくは硫酸等を添加し所望のPH値にすることを特徴とする。

【0017】本発明の作用を以下に述べる。鉄イオン濃度を高くしためっき液が混濁するのは、めっき液中の鉄イオンが空気中の酸素と反応するかもしれないめっき液中の他の成分と反応して微小な混濁物を生成するためである。そこでめっき液に添加する混濁防止剤には、まず、鉄イオンの反応を抑制すること、即ち酸化を防止する作用が必要になる。

【0018】混濁防止剤には更にめっきに用いるために以下の特性が要求される。即ち、(1)イオンに作用させるために水溶性であること、(2)混濁防止剤自体がめっき液の透明度を低下させないこと、(3)磁性めっき膜に取り込まれやすいイオンあるいは錯体を構成して磁性めっき膜の組成を変化させないこと等の条件を満たすことが望ましい。これらの条件を満たすアスコルビン酸等の有機化合物をめっき液に添加することにより、鉄イオン濃度が高くても透明度を低下させることなく、パーマロイ等の磁性めっき膜を形成することができる。さらには、分光光度計を用いてめっき液の組成を正確に測定・制御して一定な組成を有する磁性めっき膜を形成することができる。

【0019】また、混濁防止剤は、めっき液の混濁を抑制すると同時にめっき液のPHを調整する緩衝材等の機能を兼ねるものであってもよい。

【0020】

【発明の実施の形態】

(実施例1) 図1にアスコルビン酸の添加量によるめっき液透過率を、図2にこのめっき液の見かけのニッケル分析値を示す。めっき液中のニッケル=13.5 (g/L) 一定として、鉄を0.4もしくは1.8 (g/L) 添加し5時間経過しためっき液に、アスコルビン酸を20 (g/L) まで変化させて添加した。アスコルビン酸=0 (g/L) の場合、鉄=0.4 (g/L) のめっき液は混濁しないので、めっき液の透過率、ニッケル分析値に変化は起こらない。一方、鉄=1.8 (g/L) の

めっき液は混濁を起こしているため、めっき液の透過率は低く、見かけのニッケル分析値は高く出ている。アスコルビン酸を0.05 (g/L) 添加する場合、めっき液の混濁は無く見かけのニッケルの分析値はほぼ正常な値を示す。アスコルビン酸を20 (g/L) まで添加したが、透過率、見かけのニッケル分析値に変化は起こらなかった。よって、アスコルビン酸を0.05 (g/L) 以上添加することによりめっき液の混濁を取り除くことができる。

【0021】さらに、図3、図4にめっき液組成をニッケル=13.5 (g/L)、鉄=1.8 (g/L) とし、アスコルビン酸を添加してめっき液を空气中に曝し、めっき液の安定性を示す。アスコルビン酸0.05～0.5 (g/L) 添加しためっき液では、10時間程度でめっき液の透過率が低下し始めて140時間経過すると無添加の場合と同様の値となった。アスコルビン酸を1～20 (g/L) 添加しためっき液では140時間経過してもめっき液の透過率、見かけのニッケル分析値に変化ないことが判る。よって、アスコルビン酸を0.5 (g/L) を除きかつ0.5～20 (g/L) の範囲、望ましくは1～20 (g/L) の範囲で添加することにより、めっき液の長時間の混濁防止が可能である。以上、本実施例1のめっき液の成分は表1に示す。表1にはめっき液に使用した薬品とその混合量と示す。この割合で混合すると、めっき液中にはNi 13.5 (g/L)、Fe 1.8 (g/L) が溶解される。

【0022】

【表1】

薬品名	混合量 (g/L)
NiSO <sub>4</sub> · 6H <sub>2</sub> O	16.3
NiCl <sub>2</sub> · 6H <sub>2</sub> O	39.9
FeSO <sub>4</sub> · 7H <sub>2</sub> O	9.0
H <sub>3</sub> BO <sub>3</sub>	25.0
サッカリンナトリウム	1.5
アスコルビン酸	0.05～20

【0023】(実施例2) アスコルビン酸の他にめっき液の混濁防止剤として、プロトカテク酸エステル、没食子酸プロピル、没食子酸エチル、クエン酸、プロトカテク酸系化合物、没食子酸系化合物、クエン酸系化合物を利用することができる。これらの中から少なくとも一つ以上を併用してもよい。ただし、これらの有機化合物で酸化防止作用を有しながら、水溶性が良好でないために混濁防止剤に適さない有機化合物は除外する。これらの

有機化合物以外のものでも、水溶性で酸化防止作用を備える有機化合物、あるいは水溶性で鉄イオンの酸化を抑制する錯体またはイオンとして作用する有機化合物ならば本発明の混濁防止剤として利用可能である。表2において、酸化防止機能を有する有機化合物を示すが、このうち水に溶けやすいものは混濁防止剤として利用できる。

## 【0024】

## 【表2】

有機化合物

分子式

水溶性

混濁防止剤としての可否

アスコルビン酸

$C_6H_8O_6$

可溶 可

プロトカテク酸エステル

$C_9H_{10}O_4$

可溶 可

没食子酸プロピル

$C_{12}H_{13}O_2$

可溶 可

没食子酸エチル

$C_9H_{11}O_2$

可溶 可

クエン酸

$C_6H_8O_7$

可溶 可

没食子酸イソアミル

$C_{12}H_{17}O_2$

難溶 不可

ビタミンE

不溶 不可

ブチルオキシアニソール

$C_{11}H_{16}O_2$

不溶 不可

セザモール

$C_7H_6O_3$

難溶 不可

ケルセチン

$C_7H_6O_3$

不溶 不可

ジブチルオキシトルエン

$C_{15}H_{24}O$

不溶 不可

ノルジヒドログアイアレチン酸

$C_{18}H_{22}O_4$

難溶 不可

グアヤク脂

不溶 不可

【0025】（実施例3）めっき膜の形成によるめっき液のPHの変動に対して、酸性の緩衝剤を添加するめっき方法では、混濁防止剤としてアスコルビン酸のみを多量に入れすぎると、めっき液の酸性度がPH2～2.5と強くなり所望のPH値が得られなくなる。アスコルビン酸またはクエン酸もしくはアスコルビン酸とクエン酸を用いて混濁を防止すると共に、めっき液のPHが所望の値より酸性側にある場合は、水溶液が弱アルカリ性を示すクエン酸ナトリウムを添加しめっき液のPHの調整を行い、PHが所望の値よりアルカリ側にある場合は、塩酸もしくは硫酸を添加しめっき液のPHの調整をするか、アスコルビン酸をめっき液中総量で1～20 (g/L) の範囲内におさまる量を追加することで混濁を防止するとともにめっき液をPH3程度に調整することができる。

【0026】（実施例4）鉄を1.0～2.8 (g/L) の範囲で含み、あるいはニッケルと鉄の金属イオン比が(ニッケル/鉄) = 4～14の範囲内であるパーマロイ用めっき液組成を用いて磁性めっき膜のめっきを行う際に、実施例1乃至実施例3に示す混濁防止剤をめっき液に添加して、ニッケル=35～60 (wt%)、鉄=65～40 (wt%) の範囲を含有し混濁物を取り込まず、組成の一定な磁性めっき膜を得る。また、前記めっき液にコバルト、クロム、銅、モリブデンのうち少なくとも1種類以上を添加して前記磁性めっき膜を形成することにより、混濁物を含まない磁性めっき膜を形成するとともに、磁気特性を向上させてもよい。これらの一定の組成を有し混濁物を含まない磁性めっき膜を用いて、薄膜ヘッドおよびMRヘッドの磁極を形成することにより、磁極の記録磁界を増大し渦電流損を低減できる。

【0027】このような磁性めっき膜を形成するめっき装置は、磁性めっき膜を形成するウェハを固定するめっき槽と、めっき液の組成を測定する分光光度計と、めっき槽に接続されるめっき液供給管路および排出管路と、前記の二つの管路と接続してめっき液を循環させるタンクを備える。前記めっき液供給管路の一部は透明なガラス管であり、前記ガラス管は分光光度計と結合されて、めっき液の透明度とニッケル、鉄の量を測定する部分となる。前記タンクには、第一のめっき液成分NiSO<sub>4</sub>・6H<sub>2</sub>OおよびNiCl<sub>2</sub>・6H<sub>2</sub>Oの水溶液を供給する第一の容器と、第二のめっき液成分FeSO<sub>4</sub>・7H<sub>2</sub>Oの水溶液を供給する第二の容器が結合される。前記第一と第二の容器には前記タンクに対して第一、第二のめっき液成分の供給を実行・停止させるコックを有する管路がある。

【0028】上記のめっき装置において、ウェハに磁性めっき膜を形成する際に、分光光度計でめっき液の組成を正確に測定し、磁性めっき膜の形成によって低減しためっき成分を、前記第一または第二の容器から供給してめっき液の組成を一定にする。

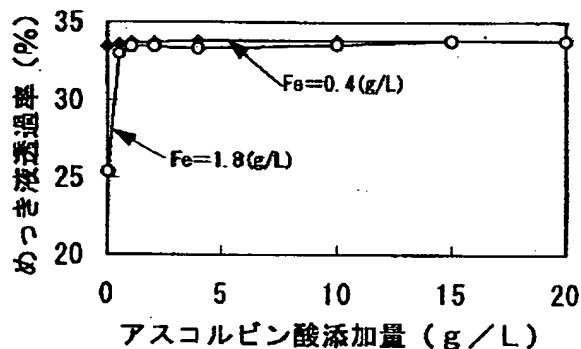
【0029】さらに、本発明は、前記第一、第二の容器のコックを電気信号によって開閉する電磁開閉弁に置き換えて、前記電気信号を前記分光光度計から送信させることにより、めっき液の自動濃度調節を行うことができる。めっき液中のニッケル濃度および鉄濃度が、求める磁性めっき膜を形成するのに不十分なほど低下する前に適切なしきい値に該当したら、前記電磁開閉弁に電気信号を送信して前記第一または第二のめっき液成分をめっき液に補充する。この補充はめっき液組成を元に戻す範囲内で行う。

【0030】

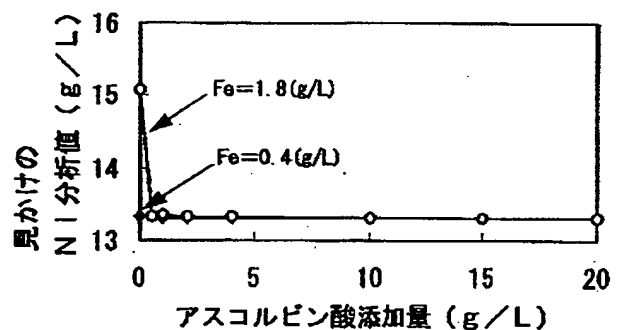
【発明の効果】本発明によれば、鉄イオンの比率が高いめっき液を用いても、めっき液の透明度の低下を混濁防止剤で抑制して、分光光度計で正確にめっき液組成を測定し、該組成を一定に保持することにより、混濁物を取り込まず、一定の組成を有するパーマロイ等の磁性めっき膜を形成することができる。

【図面の簡単な説明】

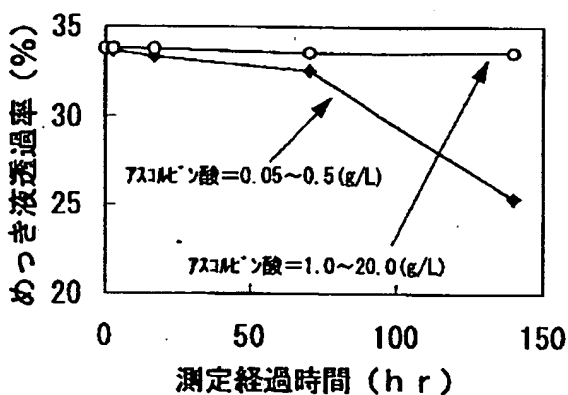
【図1】



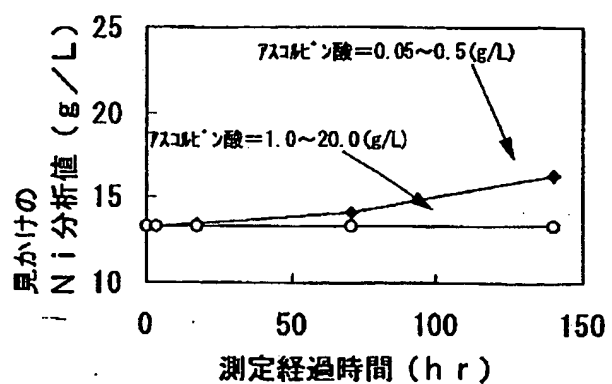
【図2】



【図3】



【図4】



【図1】本発明によるアスコルビン酸添加量とめっき液透過率の特性

【図2】本発明によるアスコルビン酸添加量と見かけのニッケル分析値の特性

【図3】本発明によるアスコルビン酸添加量に対する測定経過時間とめっき液透過率の特性

【図4】本発明によるアスコルビン酸添加量に対する測定経過時間と見かけのニッケル分析値の特性

【図5】従来のめっき液中の鉄量に対する測定経過時間とめっき液透過率の特性

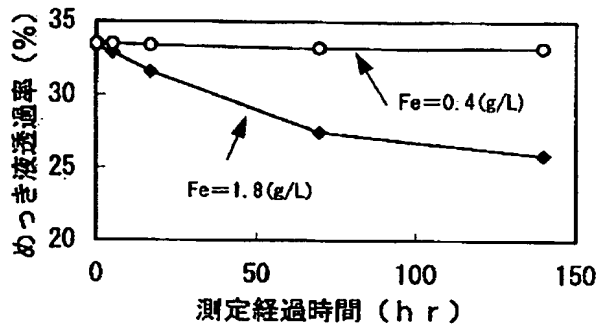
【図6】従来のめっき液中の鉄量に対する測定経過時間と見かけのニッケル分析値の特性

【図7】従来のめっき液中の鉄量とめっき液透過率の特性

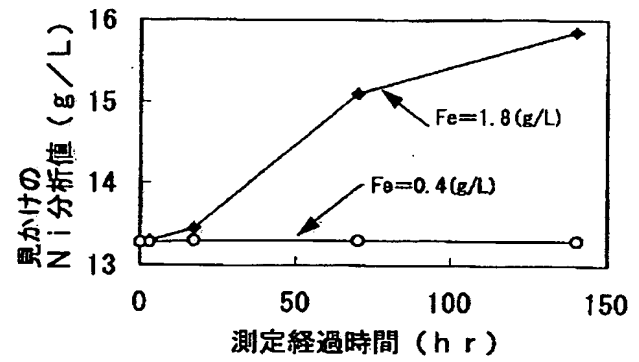
【図8】従来のめっき液中の鉄量と見かけのニッケル分析値の特性

【図9】従来のめっき液中の鉄の量とめっき膜中のニッケル分析値の特性

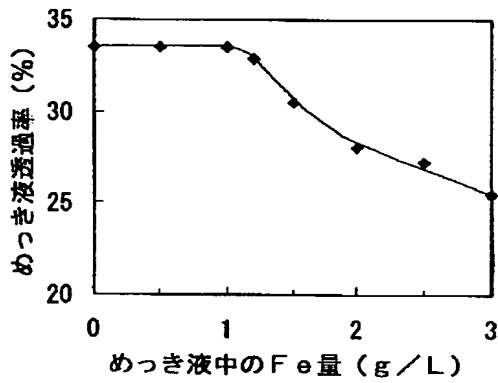
【図5】



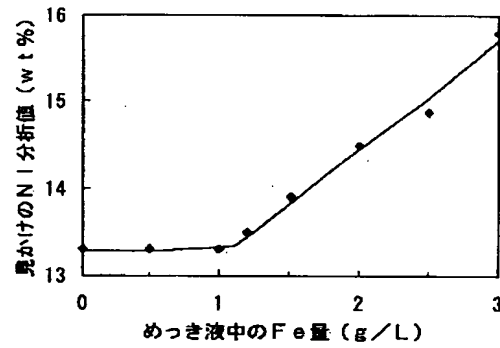
【図6】



【図7】



【図8】



【図9】

